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STUDY OF BONDING BETWEEN GLASS AND PLASTIC IN GLASS-REINFORCED
PLASTICS -- EXTENDED WORK.

By: David L. Chamberlain, Jr.

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Prepared for:

National Aeronautics and Space Administration
Lewis Research Center
2100 Brookpark Road
Cleveland, Ohio 44135

Attn: Dr. Tito Serafini

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Approved:

Lionel A. Dickinson, Director
Polymer & Propulsion Sciences Laboratory

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I INTRODUCTION

The general objective of this research program is to evaluate the effect of deliberate and known chemical bonding between the glass reinforcement and the plastic matrix of a glass-reinforced plastic composite material.

Previous reports^{1,2} described studies of the methods by which siliceous surfaces can be modified with organic groups which are bonded to surface-based silicon atoms by silicon-carbon bonds. These surface-modifying organic groups can be chosen for specific interaction with the resin matrix of the composite material. Surface modification was accomplished in two steps: (1) reactive-intermediate groups such as chlorine atoms(Cl), fluorine atoms(F), or alkoxyl groups (OR) were bonded to surface-based silicon atoms; (2) reactive-intermediate groups were converted to surface-modifying organic groups by reaction with an organo-metallic compound.

The objectives of the present phase of this project are: first, to evaluate the effects of surface modification upon a realistic composite material (such as a filament-wound NOL ring or a woven glass cloth laminate); second, to study optimum characteristics for surface modifying groups, and improved methods for obtaining them; and last, to study methods for application of surface modification to reinforcement materials other than glass and silica.

This is the first quarterly report for the current phase of work.

¹D. L. Chamberlain, Jr., Summary Technical Report No. 1, "A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase I," Contract NASr-49(14), July 31, 1964.

²D. L. Chamberlain, Jr., Summary Technical Report No. 2, "A Study of Bonding Between Glass and Plastic in Glass-Reinforced Plastics, Phase II," Contract NASr-49(14), November 15, 1965.

II EVALUATION STUDIES

Considerable time has been spent in considering methods for evaluating the effect surface modification of glass or silica fibers has on the physical properties of a composite material of practical design. Several alternate systems which can be used for this evaluation are discussed below. The questions raised in the following discussion have not been resolved, and the final evaluation route is not certain. However, the decision will be made very shortly.

NOL Rings

The NOL-interlaminar shear test method appears to be a suitable and desirable method for evaluating surface-treatment methods for glass and silica fibers. The advantages of the method are simplicity, uniformity of product, relatively few number of operations compared to other test methods, and the relatively low cost per test specimen. The disadvantages, for the purpose of the present work, are great though not insurmountable.

NOL Rings from Freshly Drawn Fibers

Ideally, the process of surface modification of fibers for NOL ring production should be carried out as the fiber leaves the bushing. For heat-sensitive glass, chlorination with phosgene or fluorine could be carried out while the fiber is cooling from the molten state. However, on the basis of present data, rates of chlorination or fluorination may be too low to permit adequate reaction at drawing speeds of 1000 ft/sec and higher. Further, the toxicity of phosgene and of fluorine requires special attention to ventilation should these reagents be used at a furnace, since it is not possible to totally enclose a short section of moving fiber.

NOL Rings from Pre-Drawn Fibers

The preparation of NOL rings from pre-drawn fibers necessitates reheating to remove lubricants and to accomplish reaction of the surface with phosgene or fluorine. The use of phosgene requires a minimum temperature of 500°C, far too high for glass fibers of any composition. The use of fluorine requires a temperature of 200°C, which may still be sufficient to cause degradation of glass fibers. Further, since the technique of chlorination is better understood than fluorination, the high-temperature process is the preferred one. Silica fibers provide an alternate material which should withstand the 500°C temperature required for chlorination. These fibers are commercially available as roving, pretreated with either of two silane "binders." According to the trade information, the binders can be removed by heating. However, for the purposes of this work, it appears unlikely that the silane binder could be completely removed without leaving a siliceous residue, and the influence of this residue upon subsequent surface-modification reactions cannot now be estimated.

Woven Cloth Laminates

Laminates can be prepared from several layers of preimpregnated glass or silica cloth from which test specimens can be prepared for conventional mechanical tests. Here again the thermal characteristics of glass fibers make the use of silica cloth more advisable. On the other hand, the binders used on silica fibers are such that the quality of the surface-modified product, and therefore the advisability of using silica cloth, may be doubtful.

III DILATOMETRIC STUDIES

Dilatometric studies were continued as a screening procedure for the effect of surface modification of silica or glass.

In continuation of the systematic evaluation of adhesion mechanisms, dilatometer strips were prepared from low-iron silica (with specific

surface of 0.21 meter²/gram) which was surface-modified with undecyl (n-C₁₁H₂₃-, straight chain aliphatic hydrocarbon) groups. The results of the dilatometer tests showed that the adhesion between a polyurethane elastomer and the undecyl-modified silica particles is less than that obtained with untreated silica or with n-butyl-modified silica. Thus, on the basis of the limited data, the adhesion between a polyurethane elastomer and surface-modified silica decreases in the order untreated > butyl-treated > undecyl-treated.

The obvious interpretation of these results is that undecyl (11-carbon atom) groups are more effective than butyl (4-carbon atom) groups in reducing the surface free energy of the silica, and that the 11-carbon atom groups are not of sufficient length to become involved in autohesive (interdiffusion) bonding with the elastomer chains.

Dilatometer specimens are now being prepared for evaluation of the autohesive effect of octadecyl groups (18 carbon atoms) on silica particles.

To date, a polyurethane elastomer has been used for dilatometer studies. This polymer has a rather high concentration of polar groups and few dangling hydrocarbons side chains, and may not participate in an autohesion mechanism as well as a strictly hydrocarbon rubber. Therefore, the materials have been collected for the preparation of a polybutadiene-acrylonitrile rubber which, hopefully, should participate more completely in the mechanism of autohesion.

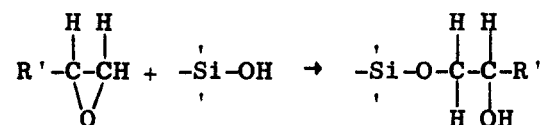
IV SURFACE MODIFICATION STUDIES

Alkoxylation and Related Reactions

Alkoxylation of silica surfaces is the process of conversion of surface-based Si-OH groups to Si-OR groups, where R is a selected organic group. Alkoxy groups have been used successfully as reactive intermediate groups for subsequent alkylation with an organometallic reagent. They also have potential utility as surface-modifying groups in their

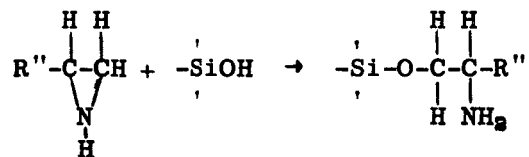
own right. Their use in promotion of bonding of siliceous surfaces to a polymer is probably restricted to environments that are not too wet, since the reactivity of the Si-OR bond to hydrolysis is high. Nonetheless, properly chosen alkoxy groups may greatly facilitate the evaluation of bonding mechanisms. Therefore, a moderate effort was applied to the study of such groups. Classically, alkoxysilane groups have been prepared from silanol groups (SiOH) by direct esterification with an alcohol (ROH) or by reaction of chlorosilane groups (Si-Cl) with an alcohol. The latter reaction is two-step, requiring a preliminary chlorination, when applied to siliceous surfaces. The former reaction liberates water, which must be removed before the reaction can be completed.

Epoxy compounds, however, provide the Si-OR linkage directly in one step.



Further, an alcohol group is simultaneously produced, thereby providing a "handle" for subsequent bonding to an epoxy, polyester, or other polymer matrix.

An extension of this type of reaction is obtained with ethylenimines, in which an amino functional group is produced.



Dodecene Oxide Reactions

Dodecene oxide, $n\text{-C}_{10}\text{H}_{21}$ $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{CH} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, was allowed to react with cleaned low-iron silica (specific surface = 0.21 meter²/gram) in the presence of boron-trifluoride-etherate catalyst. The product contained 96 ppm of carbon, as compared to none on the cleaned silica. This value

corresponds to 2 molecules of dodecene oxide per 100 \AA^2 , or a 27% conversion of surface SiOH groups.

Ethylenimine Reactions

The treatment of Cab-O-Sil (high-surface silica) with ethylenimine at room temperature and without catalyst in chloroform solution gave low coverage (about 1 molecule per 100 \AA^2 , or 12%). The same reaction carried out at 60°C gave very high loading of the silica with ethyleimine, due to polymerization of the imine.

Alkylation Studies

Routine alkylation of chlorinated low-iron silica was carried out with undecyllithium ($\text{C}_{11}\text{H}_{23}\text{-Li}$) to support the dilatometer studies.

Attempts to prepare octadecyllithium from lithium metal and octadecyl bromide were unsuccessful.

V FUTURE WORK

Major emphasis in the next quarter will be devoted to preparation and evaluation of composite materials representative of end-item structure. Simultaneously, a small effort will be devoted to developing surface-modification procedures designed to obtain maximum interaction with a subsequently applied polymer matrix. Additional data will be obtained on the rate of chlorination of glass with phosgene in order to determine the feasibility of chlorination of glass fibers as they are drawn from the bushing.

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